

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of Hajime KONDO

Application No.: 10/558,389

Filed: November 29, 2005

For: MODIFIED NATURAL RUBBER OR MODIFIED NATURAL RUBBER LATEX, AND RUBBER COMPOSITION AND PNEUMATIC TIRE

Group Art Unit: 1796

Examiner: Peter D. Mulcahy

Confirmation No.: 5714

DECLARATION UNDER 37 C.F.R. § 1.132

I, Makiko Yonemoto, declare that:

I am a co-worker of Mr. Hajime Kondo who is the inventor of the above-captioned patent application.

I received my Master of Science and Engineering from Tokyo Institute of Technology in 2004, and have been employed by Bridgestone Corporation since 2004, where I have been engaged mainly in research and development of new natural rubber.

I have made the following experiments in order to evaluate the Mooney viscosity, the ultimate strength (fracture resistance), the crack growth resistance, the $\tan \delta$ of the rubber composition comprising the modified natural rubber, which is obtained by graft-polymerizing natural rubber latex with a polar group-containing monomer and then coagulating and drying, and carbon black and/or silica, wherein a grafting ratio of the polar group-containing monomer is 0.01-5.0% by mass per the natural rubber latex, and a content of the modified natural rubber in a rubber component of the rubber composition is at least 15% by mass. Further, I have made the following experiments in order to evaluate the rolling resistance of the tire using the above rubber composition.

Experimental Procedure

<Production Example of Modified natural rubber O-1>

A modified natural rubber O-1 is obtained in the same manner as in Production Example 1 described in the present specification except that 0.6 g of 2-vinylpyridine is used instead of 3.0

g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-1 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 0.6 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is $0.6/600 = 0.1\%$.

<Production Example of Modified natural rubber O-2>

A modified natural rubber O-2 is obtained in the same manner as in Production Example 1 described in the present specification except that 3.0 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-2 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 3.0 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is $3.0/600 = 0.5\%$.

<Production Example of Modified natural rubber O-3>

A modified natural rubber O-3 is obtained in the same manner as in Production Example 1 described in the present specification except that 28.8 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-3 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 28.8 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is $28.8/600 = 4.8\%$.

<Production Example of Modified natural rubber O-4>

A modified natural rubber O-4 is obtained in the same manner as in Production Example 1 described in the present specification except that 60.0 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-4 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 60.0 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is $60.0/600 = 10\%$.

<Production Example of Modified natural rubber O-5>

A modified natural rubber O-5 is obtained in the same manner as in Production Example 1 described in the present specification except that 90.0 g of 2-vinylpyridine is used instead of

3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-5 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 90.0 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is $90.0/600 = 15\%$.

<Production Example of Modified natural rubber U-1>

A modified natural rubber U-1 is obtained in the same manner as in Production Example 1 described in the present specification except that 126.0 g of γ -methacryloxypropyl trimethoxy silane is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-1 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 126.0 g of γ -methacryloxypropyl trimethoxy silane is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is $126.0/600 = 21\%$.

<Preparation of Rubber composition>

A rubber composition is prepared by using the modified natural rubber O-1, O-2, O-3, O-4, O-5 or U-1, respectively, according to a compounding recipe shown in the following Tables A and B. With respect to the resulting rubber composition, the Mooney viscosity, the ultimate strength (fracture resistance), the crack growth resistance and the $\tan \delta$ are evaluated according to the following methods. Further, with respect to a tire prepared by using the rubber composition, the rolling resistance is evaluated according to the following method. Results are shown in Tables A and B.

(1) Mooney viscosity

For evaluating the processability of the rubber compositions, unvulcanized rubber samples were kneaded together with a vulcanized ingredient and preheated at 130°C for 1 minute using "MOONY VISCOMETER SMV201" manufactured by Shimadzu Co., Ltd., and then the rotation of the rotor was started, and the value after a lapse of 4 minute was measured as ML_{1+4} . The higher the value, the higher the unvulcanized viscosity and lower the processability or productivity.

(2) Ultimate strength (fracture resistance)

A specimen vulcanized at 160°C for 20 minutes was measured in accordance with JIS K6251-1993 to determine the tensile strength at 23°C. The higher the value, the higher the

fracture resistance.

(3) Crack growth resistance

Dumbbell-shaped specimens were punched out of a rubber composition vulcanized under vulcanization conditions at 160°C for 10 minutes, and the specimens having formed a preliminary crack of 5 mm at the center thereof were mounted on a fatigue testing machine, and subjected to strokes at 7 Hz at a constant stress, a temperature of 80°C, and a chuck distance of 20 mm, and the number of cycles necessary to a complete fracture was represented as an index on the basis that the case of Additional Comparative Example 5 is 100. The higher the value, the longer the life and the better the crack growth resistance.

(4) $\tan \delta$

Measurements were conducted on a rubber composition vulcanized under vulcanization conditions at 160°C for 14 minutes using a spectrometer (dynamic viscoelasticity measuring testing machine), at an initial load of 160 g, a frequency of 50 Hz, a strain of 1%, and a measuring temperature of 23°C. The value was represented as an index on the basis that the case of Additional Comparative Example 5 is 100. The larger the index value, the lower the loss.

(5) Rolling resistance

A rubber composition was used as the ply coating rubber, and the rolling resistance of the tire (size: 185/70R14) was measured with a drum, and the value was represented as an index on the basis that the case of Additional Comparative Example 5 is 100. The higher the value, the better the rolling resistance and the better the low rolling resistance.

Table A

	Additional Comparative Example 1	Additional Example 1	Additional Example 2	Additional Example 3	Additional Example 4	Additional Comparative Example 2	Additional Comparative Example 3	Additional Comparative Example 4
Formulation	100	-	-	-	-	-	-	-
	-	100	-	-	-	-	-	-
	-	-	100	-	-	-	-	-
	-	-	-	100	100	-	-	-
	-	-	-	-	-	100	-	-
	-	-	-	-	-	-	100	-
	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-
Results								

Table B

		Additional Comparative Example 5	Additional Comparative Example 6	Additional Comparative Example 7	Additional Comparative Example 8	Additional Comparative Example 9	Additional Comparative Example 10
Formulation	Natural rubber (grading ratio=0%)	70	70	40	20	10	-
	Modified natural rubbers O-2 (grading ratio=0.5%)	-	-	40	-	-	10
	Styrene-butadiene rubber	30	30	60	80	90	90
	Carbon Black	50	20	50	50	50	50
	Silica	-	30	-	-	-	-
	Spancile Oil	12	12	12	12	12	12
	Stearic Acid	1.5	1.5	1.5	1.5	1.5	1.5
	Zinc Oxide	4	4	4	4	4	4
	Vulcanization Accelerator	0.8	0.8	0.8	0.8	0.8	0.8
	Sulfur	3	3	3	3	3	3
	Mooney viscosity	62	82	99	56	55	54
	Ultimate strength	25	23	24	21	21	18
Results	Crack growth resistance	100	65	100	95	92	91
	tan δ	100	102	135	95	110	85
	Rolling resistance	100	100	103	99	99	97

(Summary)

As seen from Table A, when the grafting ratio of the modified natural rubber exceeds 5% by mass, the processability is largely deteriorated (i.e., Mooney viscosity increases), the ultimate strength (fracture resistance) is largely deteriorated, and the crack growth resistance is largely deteriorated.

Further, as seen from Table B, when the content of the modified natural rubber in the rubber component of the rubber composition is less than 15% by mass, the effect of improving the loss factor cannot be obtained.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 2009. 8. 10

Declarant: Makiko Yonemoto
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